

AUTOXIDATION OF HYDRAZINE

BY

PAUL HERMAN MOHR

A.B., University of Illinois, 1947

M.S., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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AUTOXIDATION OF HYDRAZINE

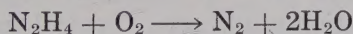
Dilute aqueous solutions of hydrazine have been found to undergo deterioration in the presence of atmospheric oxygen (1,2) and in contact with various metallic surfaces (3). The autoxidation reaction has been subjected to a more extended study a) to determine the influence of such factors as concentration of hydrazine, pH, and presence of metallic ions on the rate of oxidation and b) to develop inhibitors to stabilize hydrazine.

Hydrazine is a weak base, a polar compound, a powerful reducing agent, and a good coordinating agent. Hydrazine is also the parent substance of a system of compounds. Reactions involving hydrazine will change as the nature of the medium is varied from dilute aqueous solutions to the highly concentrated base. Hydrazine is a hydronitrogen and is being considered as a specialty fuel. It is the nitrogen analog of ethane. It is significant that hydrocarbon fuels are subject to autoxidation and that this reaction with atmospheric oxygen, leading to development of acidity and sludge formation, is catalyzed by trace quantities of various dissolved metals.

EXPERIMENTAL

A. *Autoxidation of Dilute Aqueous Hydrazine*

The oxidation of dilute aqueous hydrazine solutions by molecular oxygen was first studied by Gilbert (1) who demonstrated that the process is heterogeneous in nature and that the overall reaction may be represented by the equation:



Traces of hydrogen peroxide are formed as an intermediate product. Brown (2) subsequently found that small amounts of copper accelerate markedly the autoxidation reaction.

The author has found that copper is unique in its catalytic

action. Such metals as chromium, cobalt, nickel, manganese, and iron in the dissolved state exert little or no influence on the extent of autoxidation. The rate of the reaction appears to be some function of the dissolved copper concentration, since the percentage of hydrazine oxidized increases as the amount of added copper (as CuCl_2) is increased up to 10^{-4} M (for a 0.5 M hydrazine solution). Above this limiting concentration visible reaction results in the formation of a red precipitate of metallic copper and some cuprous oxide, presumably from disproportionation of the cuprous ion.

Both Brown (2) and Gilbert (1) had found that the autoxidation rate of dilute aqueous hydrazine solutions varies with pH and passes through a maximum at a pH equivalent to 0.01 M to 0.03 M sodium hydroxide. The author was only able to duplicate this observation when traces of copper were present.

In order to reduce the catalytic influence of copper on the autoxidation of hydrazine, the following classes of substances were evaluated:

1. Precipitating agents which form very insoluble cuprous or cupric compounds.
2. Complexing agents which coordinate strongly with the cuprous or cupric ion.
3. Adsorbents which are effective in destroying the catalytic influence of copper in other systems.

These materials were evaluated by subjecting 0.5 M hydrazine solutions containing 10^{-4} M dissolved copper and 10^{-2} M inhibitor to the action of oxygen. Typical results for the percentage of hydrazine oxidized in 24 hours under the given experimental conditions are presented in Table 1. Potassium ethylxanthate, thiourea, sodium cyanide, sodium sulfide, and sodium thiocyanate are outstanding inhibitors (copper de-activators).

TABLE 1

THE COMPARATIVE EFFECTIVENESS OF VARIOUS COPPER
DEACTIVATORS ON THE AUTOXIDATION OF DILUTE
HYDRAZINE SOLUTIONS

(Original N_2H_4 concentration: 0.500 M; deactivator
concentration: 1×10^{-2} M; Cu concentration:
 1×10^{-4} M; time: 24 hr.)

Copper Deactivator	Per Cent N_2H_4 Oxidized
Potassium ethylxanthate	4.0
Sodium stearate	8.1
Thiourea	11.2
Sodium cyanide	12.8
Sodium sulfide	13.8
Sodium thiocyanate	14.0
Ethylenediamine	20.2
Gelatin	29.6
o-Phenanthroline	31.2
Glycine	48.2
Stannic chloride	80.2
Sodium pyrophosphate	86.8
Ammonium aluminum sulfate	96.0
Mannitol	96.0
Blank	97.9

B. Autoxidation of Concentrated Hydrazine

Whereas a static procedure was employed in studying the autoxidation of dilute hydrazine solutions, a dynamic method was used throughout the investigation of the essentially anhydrous base. The observations made in the more concentrated hydrazine were found to be comparable to those obtained in the earlier investigation.

Copper was again found to be unique in its catalytic action. Such dissolved metals as chromium, vanadium, cobalt, nickel, and iron exerted no catalytic action whatsoever. It was

observed that a larger quantity of copper was capable of dissolving in the more concentrated hydrazine. Concentrations as high as 10^{-3} M cupric chloride were completely soluble in 30 M hydrazine, and no visible signs of reaction were noted until autoxidation had reduced the hydrazine concentration to approximately 7 M.

Reduction in concentration of the catalytically active copper species by the use of precipitating or complexing agents served to inhibit the autoxidation of concentrated hydrazine. The choice of inhibitor in concentrated hydrazine was, however, much more critical than in the dilute aqueous solutions. Competitive complexing action of hydrazine for the copper ion and solvolytic effects have to be taken into consideration. Copper deactivators which are particularly effective in concentrated hydrazine include sulfur, sodium sulfide, thiourea, sequestrene, sodium thiocyanate, and potassium ethylxanthate.

THE NATURE OF THE REACTION

The reaction between hydrazine and molecular oxygen is a typical autoxidation process. Hydrogen peroxide is formed as an intermediate product; the reaction is markedly catalyzed by dissolved copper, and the catalytic action can be overcome by the use of inhibitors (metal deactivators).

Several observations show evidence for the type of mechanisms involved. That the oxidation process is stepwise is indicated by the formation of trace amounts of hydrogen peroxide in the dilute aqueous solutions of hydrazine. This intermediate may be stabilized by adding small amounts of "chain breakers" (8-hydroxyquinoline and para tertiary butylcatechol). All of the dissolved copper in hydrazine solutions is present in the univalent state; in the essentially anhydrous medium the metal ion must exist primarily as the hydrazine complex. It can be postulated that the autoxidation involves a mechanism in which the copper (I) hydrazine complex participates as the catalytically active species. It is

conceivable that a copper (I)- copper (II) redox mechanism can be set up in which the copper (I) complex is oxidized to the copper (II) state and the latter is in turn promptly reduced by hydrazine to the univalent form.

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VITA

The author was born in Essen, Germany on September 17, 1920 and came to this country with his family in 1928. He attended the public schools in Buffalo, New York and was graduated from Buffalo Technical High School in 1939. In the fall of that year he enrolled in evening classes at the Millard Fillmore College at the University of Buffalo where he completed two years of undergraduate work by February 1946. During this period he was employed as Laboratory Assistant by the Linde Air Products Company in Tonawanda, New York. In the spring of 1946 he transferred to the University of Illinois where he received the degree of Bachelor of Arts in June 1947.

In the summer of 1947 he entered the graduate school at the University of Illinois and received the degree of Master of Science in June 1948. He has held the Western Cartridge Company Fellowship in Chemistry for the past two years. He is a member of Alpha Chi Sigma, the American Chemical Society, Sigma Xi, and Phi Lambda Upsilon.

He is co-author of the following publications:

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